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(54) PREPARATION OF 1,2-DICHLOROETHANE

(71) We, DYNAMIT NOBEL AKTIENGESELLSCHAFT, a German company, of 521 Troisdorf, near Cologne, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the preparation of 1,2-dichloroethane.

It is known that 1,2-dichloroethane can be prepared by introducing chlorine and ethylene in equimolar quantities into a suitable liquid medium (for example 1,2-dichloroethane itself) contained in a reactor, in the presence of a halogen transfer agent (for example iron chloride). The inert gases introduced with the chlorine gas and the hydrogen chloride formed by a secondary reaction leave the reactor as a waste gas. This waste gas contains a quantity of unreacted ethylene. This quantity of ethylene, although it may only amount to as little as 5% by weight of the ethylene used, depending upon the working conditions, is still of considerable significance so far as the economy of the process is concerned. It is not possible to reintroduce the waste gas into the reactor for further reaction since normally it only contains from 30 to at most 70% by volume of ethylene because of the presence of enriched inert gases, CO_2, N_2, O_2 and other gases.

According to the present invention, there is provided a process for the preparation of 1,2-dichloroethane, which comprises passing a gas comprising ethylene upwardly through a reactor containing a packing material against a downward flow of liquid 1,2-dichloroethane having free chlorine dissolved therein, whereby the ethylene and chlorine react to form 1,2-dichloroethane. The gas comprising ethylene can be, for example, the waste gas comprising unreacted ethylene emanating from the known process for the preparation of 1,2-dichloroethane described above, thereby reducing the loss of ethylene. The liquid medium in the known process is preferably 1,2-dichloroethane, in which case part of the 1,2-dichloroethane obtained from the reactor containing the packing material can be returned to the other reactor for use as the liquid medium.

For a better understanding of the invention, and to show how the same may be carried into effect, reference will now be made, by way of example, to the single Figure of the accompanying drawing, which is a schematic representation of an installation for the preparation of 1,2-dichloroethane.

Referring to the drawing, chlorine and ethylene are introduced through pipes L5 and L6 into a main reactor R1 containing liquid 1,2-dichloroethane in which they react to form 1,2-dichloroethane. The waste gas from the main reactor R1 is delivered through a pipe L1 into an after-reactor R2 in which it comes into contact with a stream of liquid 1,2-dichloroethane which is cycled through the after-reactor R2 by means of a pump P and which is mixed at *a* with the requisite quantity of chlorine. The ethylene present in the waste gas, *e.g.* in quantities of up to 70% by volume, is reacted until less than 5% by volume of ethylene is left in the residual gas which is removed through a pipe L4.

If necessary, the cycled 1,2-dichloroethane can be cooled by means of a condenser K so that the reaction in reactor R2 is generally carried out at temperatures of from 20 to 80°C. and preferably at temperatures of from 40 to 60°C. The pressure in reactor R2 is preferably atmospheric.

The after-reactor can be in the form of any closed vessel provided with the aforementioned pipes, for example a steel tower or tube. The after-reactor contains a packing material, *e.g.* Raschig rings, glass balls or iron rings.

The quantity of chlorine introduced at *a* is preferably not below the stoichiometric quantity required to form 1,2-dichloroethane from ethylene, although it can exceed the stoichiometric quantity, for example by 10 to 15%.

After reaction with the ethylene present in the waste gas, the chlorine-containing 1,2-

dichloroethane used as a reaction medium has too high a chlorine content for conventional purification, the chlorine content usually being from 0.004 to 0.25% by weight, more usually from 0.05 to 0.18% by weight. Accordingly, the chlorine-containing 1,2-dichloroethane which is not required for recycle is preferably returned to the main reactor R1 through a pipe L2. Its relatively high chlorine content does not present any difficulties in the reactor R1 because it can be compensated for by a corresponding reduction in the normal supply of chlorine.

In addition, the introduction of chlorine into the main reactor R1 can be throttled to such an extent that hardly any excess chlorine can be detected in the crude of 1,2-dichloroethane leaving the main reactor R1 through pipe L3. For example, the stoichiometric excess of ethylene with respect to chlorine fed to the main reactor R1 by pipes L5 and L6 can be from 2.9 to 7.4%, preferably from 3.5 to 6.5%. The resulting increasing ethylene content of the waste gas leaving the main reactor through the pipe L1 does not matter because, in accordance with the invention, it is reacted in the after-reactor R2 to form 1,2-dichloroethane. The waste gas delivered through pipe L1 usually contains from 10 to 70% by volume of ethylene, more usually from 30 to 60% by volume of ethylene.

In order to be able to carry out the process with maximum economy, it is best continuously to measure the residual ethylene content of the residual gas leaving the after-reactor R2 through the pipe L4 by suitable methods, for example by means of an infrared spectrograph. Addition of chlorine at *a* can thus be controlled on the basis of the results obtained. In this way, it is possible for example to react waste gases containing from 10 to 70% by volume of ethylene with 1,2-dichloroethane containing from 0.1 to 0.6% by weight of chlorine in a yield that is extremely high for a liquid phase reaction and, in spite of this, to obtain a 1,2-dichloroethane substantially free from chlorine as the reaction product.

The invention will now be illustrated by the following Examples, wherein the apparatus described above with reference to the drawing was used.

EXAMPLE 1

A waste gas of the following composition:

3.6% volume of HCl
20.5% by volume of CO_2
0.5% by volume of CO
3.6% by volume of 1,2-dichloroethane
11.8% by volume of N_2+O_2
60.0% by volume of ethylene

issuing from reactor R1 at rate of 170 m^3/h was introduced through the pipe L1 into the after-reactor R2 packed with Raschig rings. In this after-reactor, the gas was contacted countercurrently at 50 to 80°C. with 87.5 metric tons/hour of liquid 1,2-dichloroethane having dissolved therein 0.35% by weight of free chlorine. After reaction with the waste gas, the 1,2-dichloroethane still contained 68 ppm of free chlorine whilst the residual gas leaving the after-reactor R2 through the pipe L4 had the following composition:

5.3% by volume of HCl
35.0% by volume of CO_2
0.6% by volume of CO
2.9% by volume of 1,2-dichloroethane
53.8% by volume of N_2+O_2
2.4% by volume of ethylene.

The excess 1,2-dichloroethane formed was removed from the circuit before the condenser K and introduced into the reactor R1 at its lower end. The 1,2-dichloroethane leaving the reactor R1 through the pipe L3 had a residual content of free dissolved chlorine of only 21 ppm.

EXAMPLE 2

A waste gas of the following composition:

2.7% by volume of HCl
15.5% by volume of CO_2
0.5% by volume of CO
2.6% by volume of 1,2-dichloroethane
19.7% by volume of N_2+O_2
59.0% by volume of ethylene

issuing from Reactor R1 at a rate of 280 m^3/h was introduced into the after-reactor R2 through the pipe L1. In the after-reactor R2, the gas was contacted counter-currently at 50 to 80°C. with 100 metric tons/hour of liquid, 1,2-dichloroethane having dissolved therein 0.5% by weight of free chlorine. After reaction with the waste gas, the 1,2-dichloroethane still contained 57 ppm of free chlorine whilst the residual gas leaving the after-reactor R2 through the pipe L4 had the following composition:

4.0% by volume of HCl
30.5% by volume of CO_2
0.6% by volume of CO
2.2% by volume of 1,2-dichloroethane
58.4% by volume of N_2/O_2
4.3% by volume of ethylene.

WHAT WE CLAIM IS:—

1. A process for the preparation of 1,2-dichloroethane, which comprises passing a gas comprising ethylene upwardly through a reactor containing a packing material against a downward flow of liquid 1,2-dichloroethane having free chlorine dissolved therein, where-

by the ethylene and chlorine react to form 1,2-dichloroethane.

2. A process according to claim 1, in which the ethylene and chlorine react at a temperature of from 20 to 80°C.

3. A process according to claim 1 or 2, in which the gas contains from 10 to 70% by volume of ethylene.

4. A process according to claim 1, 2 or 3, in which the liquid 1,2-dichloroethane has from 0.1 to 0.6% by weight of free chlorine dissolved therein.

5. A process according to any one of the preceding claims, in which the amount of free chlorine dissolved in the liquid 1,2-dichloroethane is not less than the stoichiometric amount required to react the ethylene to form 1,2-dichloroethane.

6. A process according to claim 5, in which the amount of free chlorine dissolved in the liquid 1,2-dichloroethane exceeds the stoichiometric amount required to react with the ethylene to form 1,2-dichloroethane by up to 15%.

7. A process according to any one of the preceding claims, in which the gas comprising ethylene is the waste gas comprising unreacted ethylene emanating from the preparation of 1,2-dichloroethane by introducing chlorine and ethylene into a liquid medium contained in another reactor.

8. A process according to claim 7, in which the liquid medium is 1,2-dichloroethane.

9. A process according to claim 7, in which part of the 1,2-dichloroethane obtained from the reactor containing the packing material is returned to the other reactor for use as the liquid medium.

10. A process according to claim 9, in which the chlorine content of the 1,2-dichloroethane returned to the other reactor is from 0.004 to 0.25% by weight.

11. A process according to any one of claims 7 to 10, in which the amount of ethylene introduced into the liquid medium exceeds the amount of chlorine introduced into the liquid medium, the excess, stoichiometrically, being from 2.9 to 7.4%.

12. A process according to claim 1 for the preparation of 1,2-dichloroethane, substantially as hereinbefore described with reference to the accompanying drawing.

13. A process for the preparation of 1,2-dichloroethane, substantially as described in either one of the foregoing Examples.

14. 1,2-Dichloroethane whenever obtained by the process claimed in any one of the preceding claims.

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1405926 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*